COMPUTATIONAL MODELS TO DETERMINE TRANSPORT AND HYDROLYSIS RATE PARAMETERS OF CONTAMINANTS IN A WATER DISTRIBUTION SYSTEM

Mark D.Ginsberg,[1] Margaret M. Hurley,[2] Aleksei Aksimentiev,[3]
Frances C. Hill,[4] and Vincent F. Hock[1]

[1]U. S. Army Engineer Research and Development Center, Champaign, IL 61821
[2]US Army Research Laboratory, Aberdeen Proving Ground, MD 21005
[3]Department of Physics, University of Illinois, Urbana, IL 61801
[4]U. S. Army Engineer Research and Development Center, Vicksburg, MS 39180

ABSTRACT

The anthrax attacks of September 18, 2001 refocused attention on methods of asymmetric warfare including introduction of contaminants into water distribution systems. To predict the outcome of such an event, previous chemical models of transport in water distribution systems assumed that any contaminant would move through the system via pure hydraulic transport, meaning that the contaminant would not interact with the pipe wall. Such models predict that flushing a system with uncontaminated water would clear away contaminants fairly rapidly. Previous field experience with actual contamination events (O'Brien, 2003) showed that flushing contaminants was quite slow and difficult in practice. For example, in 1980, a chlordane contamination event in Pittsburgh, PA required a flushing program of 8 months duration for 2000 affected customers. For military installations, such a long delay represents an intolerable risk to mission capability (Hock et al., 2005; Ginsberg and Hock, 2004). The research described uses computational chemistry to calculate, *ab-initio*, time constants associated with sorption, desorption, and hydrolysis using only selective verification by empirical methods. The computational methods used include: molecular dynamics using NAnoscale Molecular Dynamics (NAMD) to describe sorption and desorption, Turbomol and Cosmotherm to obtain correlations to molecular morphology that are less computationally expensive than NAMD, and density functional theory (DFT) combined with the polarizable continuum model (PCM) in Gaussian03 to predict reaction rates of hydrolysis.

1. INTRODUCTION

In previous research, empirical methods showed that uptake of contaminant on pipe material was a function of the contaminant's hydrophobicity, molecular weight, and number of contact points with the pipe surface. Fate and transport are also dependent on the rate of hydrolysis of contaminant in the water distribution environment, including interaction with chlorination. This new detailed knowledge of fate and transport of contaminants in water distribution systems indicated that it is feasible to use computational methods to directly calculate the time constants associated with uptake and hydrolysis using only selective verification by empirical methods. All methods are validated with laboratory measurements (Ginsberg and Hock, 2004; Ginsberg et al., 2005)

2. EXPERIMENTAL RESULTS

Previous laboratory results showed that uptake of contaminant on pipe surfaces is characterized by thermodynamic partition, where a fixed fraction of the contaminant available sorbs to the pipe material. The rate of interaction is a first order relaxation to an asymptotic equilibrium uptake. As such it is characterized by the asymptotic fraction 'β' (on a scale of 0 for no uptake, to 1 for complete uptake), and an exponential time constant 'T'. Laboratory measurements are being conducted on several combinations of (CB) contaminants and pipe material. The results indicate that the interaction between pipe wall and contaminant can be quite strong. As an example, Figure 1 shows the asymptotic uptake of prophos (a commercially available nematacide) on concrete-lined ductile-iron pipe with an asphaltic sealer coat is 100% at an exponential relaxation time constant of 77 hours (i.e., β=1 and T=77 hours). As 77 hours is comparable to the total transport time of water within a distribution system, the expected effect under field conditions would be quite strong.

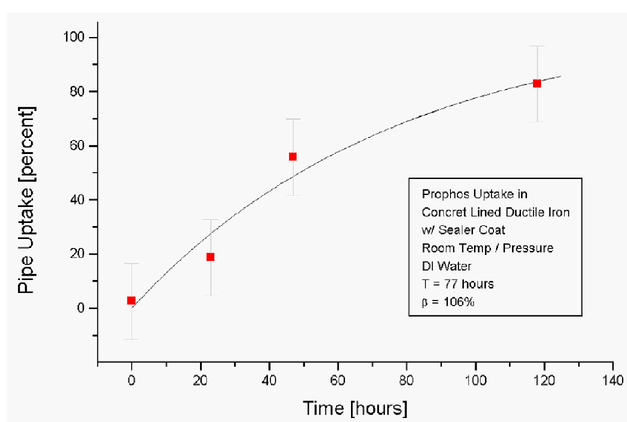

Figure 1. Experimental result showing aggressive uptake of prophos in concrete-lined pipe with an asphaltic sealer coat.

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3. MOLECULAR DYNAMICS (MD) STUDY OF FLOW-INDUCED SORPTION/DESORPTION.

To understand the microscopic mechanism of contaminant interaction with the pipe surfaces we performed MD simulations of water/pipe/contaminant systems. MD is a computational method that allows the microscopic dynamics of a molecular system to be modeled at atomic resolution. In this method, a molecular system is approximated by an ensemble of virtual atoms interacting with each other according to a complex potential function – the molecular force field (Allen and Tildesley, 1987), which has been developed and calibrated to quantitatively reproduce the physical properties of a simulated system. The trajectory of each atom is obtained by integrating Newton's equation of motion. The potential energy function describing the interactions of all atoms in the system is derived from quantum-mechanics calculations and is further refined to reproduce physical properties of the simulated system.

For our test simulations of flow-induced soption/desorption we used Dimethyl Methylphosphonate (DMMP) as a prototypical organophosphate contaminant. As no force field for DMMP consistent with our model of water and silica was available, we have adapted the force field parameters for DMMP based on its rigid-bond model (Vishnyakov and Neimark 2004), additional parameters from (Barvík et al., 2002) and the CHARMM force field (MacKerell 1998). The obtained parameters were tested by repeating simulations using a method reported in Vishnyakov and Neimark (2004).

As a model of typical surfaces found in a cement pipe, we used an all-atom model of amorphous silica that accurately reproduces atomic-scale roughness of the surface and its wetting properties (Cruz-Chu et al., 2006). The interactions between water and silicon dioxide were calibrated by measuring a water contact angle (WCA), the angle between the tangent of a sessile water droplet and the solid surface (Werder et al., 2003). The silica surfaces were obtained using numerical procedures that mimic experimental annealing, varying the heating and quenching rates. The force field parameters describing the interactions of water and silica were calibrated to reproduce the experimental dependence of the WCA on the number of dangling atoms at the surface, the latter being controlled by the annealing cycle. Thus, our model is a close representation of the real surface, providing a good compromise between the heterogeneity of amorphous silica and the magnitude of the intermolecular forces. For our studies of flow-induced sorption/desorption, we used silica surfaces of the following two types: an atomically flat hydrophilic surface containing a large number of dangling atoms, and an annealed hydrophobic surface that had no dangling atoms but had a considerable atomic-scale roughness (Figure 3).

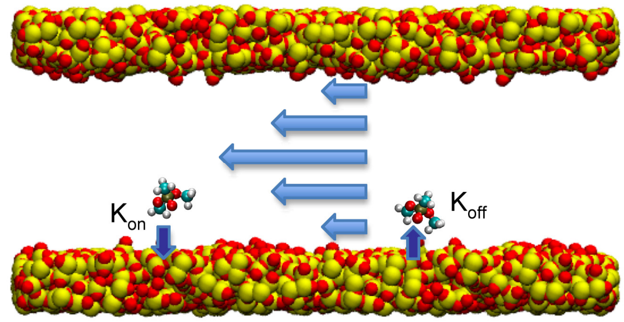

Figure 2. Molecular dynamics simulations of flow-induced sorption/desorption of DMMP.

A typical simulation system, shown in Fig. 2, contained an aqueous solution of DMMP placed between two rectangular slabs of silica. MD simulations were performed using NAMD (Phillips et al., 2005), periodic boundary conditions, and full electrostatics. Other simulation conditions and protocols used were as described in (Aksimentiev et al., 2004). To induce a flow of water through the channels, each water molecule was subject to a constant force '*F'* directed along the desired water direction. For a system with '*N'* atoms, this creates a pressure difference, $\Delta P = NF/A$, where '*A'* is the cross-section of the channel.

To test if the character of the silica surface can influence the uptake of the contaminants, flow-induced simulations were performed through channels having hydrophobic and hydrophilic surfaces. As the mixture of DMMP and water was pushed to flow through the channels, DMMP molecules were observed to interact with the channel's surfaces; some of those interactions led to DMMP binding. After 10 ns of MD, both systems reached a quasi-stationary state. Figure 3 shows the results of these simulations. In the hydrophilic channel, about 70% of the contaminant adsorbed to the surface; the DMMP molecules were observed to bind to and unbind from the surface in a dynamic equilibrium state. In the hydrophobic channel, all contaminant molecules adsorbed to the surface after about 10 ns simulation. This dramatic influence of the surface properties on the update of organophosphate contaminants suggests that the latter may be controlled though surface treatment.

These simulations demonstrated the feasibility of using the MD method to quantitatively characterize sorption/desorption phenomena in a flow through a channel. Future studies will be directed toward computing the rates of sorption/desorption, characterizing the influence of the surface heterogeneity on the contaminant binding, comparative studies of binding kinetics of difference contaminants and on extending this methodology to modeling adsorption of biomacromolecules.

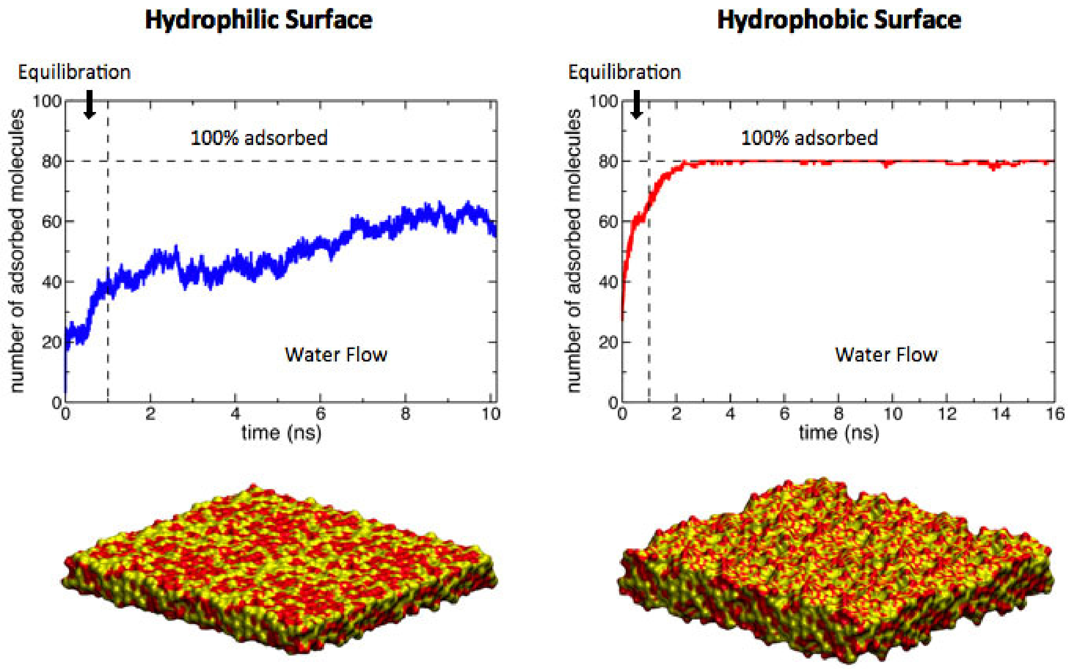

Figure 3. Surface properties affect the uptake of DPPM. The number of DMMP molecules adsorbed at the hydrophilic (left) and hydrophobic (right) surfaces is plotted versus simulation time. The snapshots at the bottom illustrate the two model surfaces used.

4. COMPUTATIONAL CHARACTERIZATION USING TURBOMOL AND COSMOTHERM

The theory of adsorption has far-reaching applications within the scientific and engineering community. One branch of this theory which has received much interest within the last decade has been developed within framework of the conductor-like screening (COSMO-RS) model (Klamt and Schüürmann, 1993; Klamt, 1995; Andzelm et al., 1995; Maaßen et al., 1995). This theory, which combines aspects of quantum theory, dielectric continuum theory and statistical thermodynamics, was originally developed for fluid phase property prediction. However, the authors were quick to grasp the possibilities of extension to partitioning complex systems, and applications ranging from intestinal adsorption to soil sorption to adsorption on activated carbon rapidly ensued. This portion of the project follows within the spirit of this development, and attempts to apply a similar methodology to explain partitioning of water-borne contaminants between the aqueous phase and the pipe wall. The basis of this model is in the surface polarization charge density (Figure 4). This quantity is known to be a very good local measure of polarity and therefore correlate strongly with a chemical's response to its environment at the molecular level. More general forms of the method require a minimum of fitted parameters and generation of the profile for all compounds involved in the case of a standard miscibility or partitioning scenario, such as the octanol-water partition coefficient. In the case of adsorption to a solid surface, less direct means may be used, which involve more mathematical fitting to sufficient quantities of data. The chemical (and to some extent structural) features of the pipe walls of interest for this project are largely unknown, and for this reason a mathematical fit will be attempted.

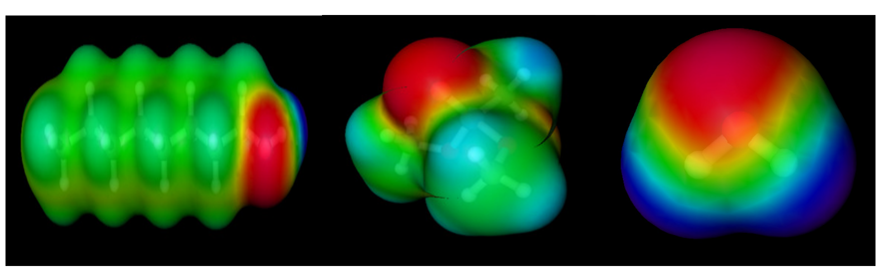

Figure 4. Polarity maps of the molecules: 1-octanol, DMMP, and water. The intense red and blue areas are polar, green is non-polar.

5. COMPUTATIONAL PREDICTIONS OF HYDROLYSIS IN POTABLE WATER

Ab-initio quantum chemical techniques were used to investigate the degradation mechanism of a representative organophosphate, Phosphonothioic acid, in water. Calculations using the Density Functional Theory (DFT) approach

and the B3LYP exchange and correlations functionals were performed to optimize the structure of an organophosphate in the gas phase and in water (Figure 5). The Polarizable Continuum Model (PCM) approach available in the Gaussian03 (Frisch et al, 2004) suite of programs was used to simulate the solvent water.

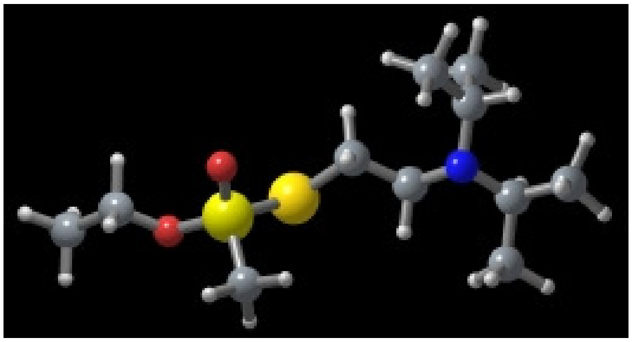

Figure 5. Optimized structure of an organophosphate.

Previous studies on the hydrolysis of phosphinate, phosphonate and phosphate molecules showed that good accu-racy was obtained using this method and a 6-31+G(2d,2p) basis set (Wright et al, 2005), and this basis was used in the ensuing calculations. Tight convergence criteria were used throughout the study. The geometry obtained from the optimization in water was used as a starting point for the hydrolysis reaction. Verification that a transition state was obtained in the degradation pathway was obtained by carefully tracing the reaction path in both directions from the transition structure. The predicted mechanism shows that an OH- group from a water molecule approaches the phosphonate group opposite to the fluoride leaving group through an SN2-type reaction. Competition exists between a breaking of the P-S bond and a breaking of the P-OEt bond in the phosphonate group, as has been observed by Daniel et al. (2008). We are currently working to determine the complete energetics of the system, and to determine reaction rates for the competing cleavage reactions.

6. DISCUSSION

The computational methods summarized here represent several advances in computational chemistry as applied to infrastructure: 1.) These computational tools are inexpensive compared to using purely empirical methods to obtain the same results. 2.) Although the theory behind scaling from nano-scale interactions between contaminants and pipe surfaces has been, in principle, settled by the statistical view of thermal physics, the ability to make the connection between forces measured in molecular computer simulations and the Gibbs free energy is relatively recent. (ex. Roux, 2002) 3.) Once the results are understood for the computationally intensive studies using molecular dynamics and density functional theory, correlation studies may show how to obtain the same results with tools like Turbomol / COSMOtherm using more modest computer resources.

This research also establishes a scientific basis for subsequent technical improvements in military and civilian simulation capabilities. The time constants and partition coefficients will be embedded in current hydraulic simulations tools (models) such as EPANet or Aquis. It represents the first research to predict the strong interactions between chemical contaminants and commonly used pipe material. The improved fidelity of the models underlying water distribution simulations will provide the Army with improved tools for vulnerability assessment, emergency response planning, and infrastructure planning. Immediate military applications also include development of risk assessment models for force projection and for critical fixed facilities (e.g., military hospitals).

Beyond its military applications, this research effort contributes substantially to the national welfare. In civilian applications, the improved simulation capability will assist better formulation of capital improvement plans, facility protection methods, and emergency response strategies for iconic structures and vulnerable fixed facilities (e.g., food manufacturing, judicial, and governmental functions). This helps formulate immediate response strategies for water-borne attacks such as those already attempted by terrorist groups.

7. CONCLUSION

The research being conducted shows that three principle computational approaches, applied in a synergistic way and with empirical validation, are being used to determine the fate and transport constants of contaminants in a water distribution system. Sorption of contaminants on pipe material can be simulated using molecular dynamics. Hydrolysis rates are determined using a combination of density functional theory and the polarizable continuum model. Both sets of computational results may later be extended by demonstrating that they correlated to less computationally intensive methods such as Turbomol / COSMOtherm. The fate and transport constants, in turn, can provide new simulation tools that can enhance vulnerability assessment methods, emergency response planning, infrastructure planning, and system operation.

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